United States Patent Office

3,513,182

Patented May 19, 1970

3,513,182

BICYCLIC-SUBSTITUTED SULFAMIDES

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No Drawing. Filed July 18, 1966, Ser. No. 565,673
Claims priority, application Germany, July 24, 1965, F 46,710
Int. Cl. A01n 9/16; C07c 143/80
U.S. Cl. 260—453 10 Claims

ABSTRACT OF THE DISCLOSURE

[(Optionally mono- to tri- methyl substituted)-bicyclo-(2,2,1 and 2,2,2)-alkyl-(C_{0-2} alkyl)]-substituted-[N-(optionally alkyl substituted)-N'-(optionally alkyl and alkoxy substituted)-N'-(alkyl)]-sulfamides which possess pest repellant properties and which may be prepared by conventional methods.

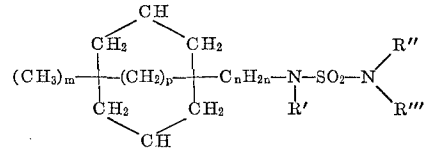
The present invention relates to particular new bicyclic-substituted sulfamides, which surprisingly possess strong pest-repellent, especially insect- and mite-repellent, properties, to their compositions with dispersible carrier vehicles, and to methods for the production and use thereof.

It is already known that dimethyl phthalate (A) can be used as an insect repellent. This compound has already attained a substantial significance in practice although it possesses a repellent activity which only lasts for several hours.

It is an object of the present invention to provide certain particular new bicyclic-substituted sulfamides which possess valuable pest-repellent, and especially arthropod-repellent such as insect-repellent and mite-repellent, properties to provide active compositions in the form of mixtures of such compounds with dispersible liquid and solid carrier vehicles; and to provide methods of using such components in a new way, especially for repelling pests, such as arthropods, and the like.

Other and further objects of the present invention will become apparent from a study of the within specification and accompanying examples.

It has now been found in accordance with the present invention that the particular bicyclic-substituted sulfamides having the formula:



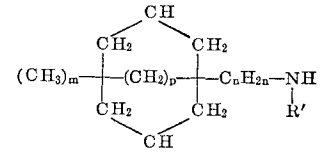
(I)

in which m is a number from 0 to 3, p is a number from 1 to 2, n is a number from 0 to 2, R' is selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, R'' is selected from the group consisting of hydrogen, alkyl having 1 to 4 carbon atoms, and alkoxy having 1 to 3 carbon atoms, and R''' is alkyl having 1 to 4 carbon atoms, possess strong pest-repellent, and especially insect- and mite-repellent, properties.

It is very surprising that the particular new active compounds usable according to the present invention have a substantially higher repellent action against pests, such as insects and mites, than previously known insect-repellent compounds such as dimethyl phthalate (A). The particular active compounds usable according to the present invention thus represent a valuable addition to the art.

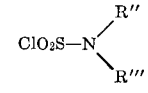
The particular new active compounds according to the present invention can be prepared by numerous known processes.

Thus, the instant new compounds can be prepared by the process which comprises reacting bicyclically-substituted amines of the general formula:



(IIa)

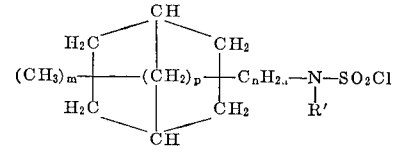
in which R', m, n, and p are the same as defined above, with sulfamic acid chlorides of the general formula:



(IIb)

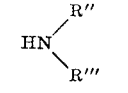
in which R'' and R''' are the same as defined above.

The particular new compounds of general Formula I above can also be obtained by the process which comprises reacting bicyclically-substituted sulfamic acid chlorides of the general formula:



(IIc)

in which R', m, n and p are the same as defined above, with amines of the general formula:



(IId)

in which R'' and R''' are the same as defined above.

Examples of bicyclically-substituted amines of general Formula II*a* which can be used for the reaction and which are readily obtainable, for example, from diene addition products, and some also from natural substances, include the following: 2-bicyclo-[2,2,1]-heptyl-amine, 2-bicyclo-[2,2,1]-heptyl-methylamine, 1- and 2-(2-bicyclo-[2,2,1]-heptyl-ethylamine, fenchylamine, bornyl-amine, isobornylamine, 2-amino-isocamphane, N-methyl-bornylamine, and (2-methyl-bicyclo-[2,2,1]-heptyl-2)-methylamine.

The amines of general Formula IId are known. The following may be mentioned, by way of example: methyl-amine, dimethylamine, methyl-ethylamine, diethylamine, isopropylamine, n-butylamine, isobutylamine, tert.-butyl-amine, di-n-butylamine, methyl-butylamine, di-n-propyl-amine, methyl-butylamine, di-isobutylamine, N,O-dimeth-yl-hydroxylamine and N,O-diethyl-hydroxylamine.

The sulfamic acid chlorides of general Formula IIc usable for the reaction with the amines of general Formula IId are derived from the above amines of general Formula IIa and can be prepared from the latter in known manner, for example, by reaction with sulfuryl chloride.

The sulfamic acid chlorides of general Formula IIb are known.

In the production of the instant compounds of Formula I by one of the two above-mentioned processes, it is advantageous to use solvents, such as aromatic hydrocarbons, ethers, ketones and esters, and acid-binding agents, such as triethylamine, pyridine, sodium carbonate or sodium hydroxide.

The reaction temperatures used are preferably between about 0 and 100° C.

The reactions are expediently carried out with approxi-

mately equimolar amounts of the reaction components, in the presence of at least the equivalent amount of an acid-binding agent and in the simultaneous presence of a solvent. The acid-binding agents may also be replaced by an excess of the corresponding amine component. Working up is carried out in conventional manner.

The particular new compounds according to the present invention advantageously exhibit a strong repellent action against arthropods, and a low toxicity toward warm-blooded animals. The effect lasts a long time. The instant compounds can, therefore, be used, with good results, for repelling obnoxious sucking and biting insects and mites.

The sucking insects contemplated herein essentially include mosquitoes, such as the species Aedes, Culex and Anopheles; sand flies such as Phlebotomes; biting flies, such as Culicoides species; buffalo gnats, such as the Simulium types; stinging flies, such as the stable fly (*Stomoxys calcitrans*), the tsetse flies (*Glossina* species), horse flies, such as the Tabanus, Haemotopota and Chrysops species; the housefly (*Musca domestica*); the lesser housefly (*Fannia canicularis*); the meat flies, such as *Sarcophaga carnaria*; flies causing myiasis such as *Lucilia cuprina, Chrysomyia chloropyga, Hypoderma bovis, Hypoderma lineata, Dermatobia hominis, Oestrus ovis, Gasterophilus intestinalis* and *Cochliomyia hominivorax;* bugs, such as *Cimex lectularius, Rhodnius prolixus* and *Triatoma infestanes;* lice, such as *Pediculus humanus, Haematopinus suis* and *Damalinia ovis;* keds, such as *Melophagus ovinus;* fleas, such as the human flea (*Pulex irritans*) and *Ctenocephalus canis,* and sand fleas, such as *Dermatophilus penetrans;* and the like.

The biting insects contemplated herein essentially include cockroaches, such as the German cockroach (*Blattella germanica*), the oriental beetle (*Blatta orientalis*); beetles, such as the grain weevil (*Sitophilus granarius*), the stag beetle (*Hylotrupes bajulus*), the death watch beetle (*Anobium punctatum*), the leather beetle (*Dermestes lardarium*), the mealworm beetle (*Tenebrio molitor*) and termites, such as *Reticulitermes lucifugus*; and ants, such as *Lasius niger*; and the like.

The mites contemplated herein include ticks, such as *Ornithodoros moubata, Boophilus microplus* and *Amblyomma hebraeum,* and mites in the stricter sense, such as *Dermanyssus gallinae* and *Sarcoptes scabiei*; and the like.

Thus, the active compounds of the instant invention can be used as pest-repellents either alone or in admixture with solid or liquid carriers or diluents.

The active compounds according to the instant invention can be utilized, if desired, in the form of the usual formulations or compositions with dispersible carrier vehicles, such as solutions, emulsions, suspenion, emulifiable concentrates, spray powders, pastes, soluble powders, dusting agents, granulates, ointments, oils, lacquers, sprays, etc. These are prepared in known manner, for instance by extending the active agents with dispersible liquid diluent carriers and/or dispersible solid carriers optionally with the use of carrier vehicle assistants, e.g., surface-active agents, including emulsifying agents and/or dispersing agents, whereby, for example, in the case where water is used as diluent, organic solvents may be added as auxiliary solvents (cf. Agricultural Chemicals, March 1960, pages 35–38). The following may be chiefly considered for use as carrier vehicles for this purpose: dispersible liquid diluent carriers, such as aromatic hydrocarbons (for instance, benzene, toluene, xylene, etc.), halogenated, especially chlorinated, aromatic hydrocarbons (for instance, chlorobenzenes), paraffins (for instance, petroleum fractions), chlorinated aliphatic hydrocarbons (for instance, methylene chloride, etc.), alcohols (for instance, methanol, ethanol, propanol, butanol, etc.), animal and vegetable fats (for instance, lanolin, olive oil, nut oils, etc.), amines (for instance, ethanolamine, etc.), amides (for instance, dimethyl formamide, etc.), sulfoxides (for instance, dimethyl sulfoxide, etc.), ketones (for instance, acetone, etc.), and water; as well as dispersible finely divided solid carriers, such as ground natural minerals (for instance, kaolins, alumina, silica, chalk i.e., calcium carbonate, talc, kieselguhr, etc.) and ground synthetic minerals (for instance, highly dispersed silic acid, silicates, e.g., alkali silicates, etc.); whereas the following may be chiefly considered for use as carrier vehicle assistants, e.g., surface-active agents, for this purpose: emulsifying agents, such as non-ionic and anionic emulsifying agents (for instance, polyethylene oxide esters or fatty acids, polyethylene oxide ethers of fatty alcohols, alkyl sulfonates, aryl sulfonates, etc., and especially alkyl aryl-polyglycol ethers, magnesium stearate, sodium oleate, etc.); and dispersing agents, such as lignin, sulfite waste liquors, methyl cellulose, etc.

As will be appreciated by the artisan, the active compounds according to the instant invention may be present in such formulations or compositions in the form of mixtures with one another and with other known active substances, if desired.

The substances according to the invention may be employed by themselves as the artisan will appreciate, in the form of their compositions with solid or liquid dispersible carrier vehicles or other known compatible active agents, or in the form of particular dosage preparations for specific application made therefrom, such as solutions, emulsions, suspensions, powders, pastes, ointments, oils, lacquers, sprays, and granulate which are thus ready for use.

As concerns commercially marketed preparations, these generally contemplate carrier composition mixtures in which the active compound is present in an amount substantially between about 0.1–95% by weight, and preferably 0.5–90% by weight of the mixture, whereas carrier composition mixtures suitable for direct application or field application generally contemplate those in which the active compound is present in an amount substantially between about 0.01 and 95%, preferably 0.1 and 80%, by weight of the mixture. Thus, the present invention contemplates over-all compositions which comprise mixtures of a dispersible carrier vehicle, such as (1) a dispersible carrier solid, or (2) a dispersible carrier liquid preferably including a carrier vehicle assistant, e.g., surface-active agent, such as an emulsifying agent and/or a dispersing agent, and an amount of the active compound whic his effective for the purpose in question and which is generally between about 0.01 and 95% by weight of the mixture.

Furthermore, the present invention contemplates methods of repelling pests, especially insects and acarids, such as mites, which comprise applying to at least one of (a) such pests and (b) their habitat, a pest-repellent, especially insect-repellent and/or acarid-repellent, such as mite-repellent, effective amount of the particular active compound of the invention alone or together with a carrier vehicle, as noted above. The instant formulations or compositions are applied in the usual manner, for example, by spraying, atomizing, vaporizing, scattering dusting, watering, sprinkling, pouring, rubbing, and the like.

It will be realized in accordance with the present invention that the instant compounds may be used effectively not only in plant protection but also generally against insects and acarids, specifically for protection against insects and mites.

Advantageously, for protection against blood-sucking insects and mites, the active compounds are applied to human or animal skin, or clothes or other articles are impregnated with them. To repel pests damaging foodstuffs or materials, the substances to be protected are either treated directly with the instant active agents or the latter are applied to an area around the substances to be protected, thus creating inhibition zones against the penetration of the pests.

The following example is given by way of illustration, and without limitation, of utility of the particular new compounds according to the present invention:

EXAMPLE 1

Repellent test/mosquitoes
Test insect: *Aedes aegypti*
Solvent: alcohol

To produce a suitable preparation of the particular active compound, 5 parts by weight of such active compound are mixed with 100 parts by volume of the stated solvent.

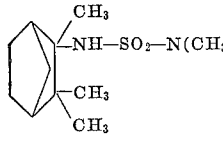
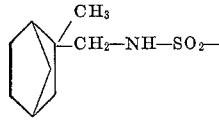
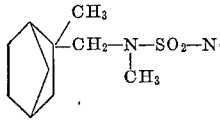
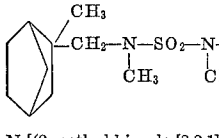
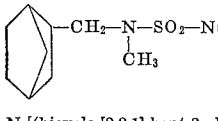
A patch of hair is shaven off from the backs of guinea pigs to the extent of 50 cm.^{2}. 0.4 cc. of the resulting preparation of the given active compound are uniformly distributed over this shaven area. The animals are then placed in narrow cages of fine wire mesh which leaves free the shaven area of the back of the respective animal. The cages containing the guinea pigs are placed for 10 minutes in larger cages containing several thousand hungry mosquitoes flying about. Of course, while the mesh of the narrow cages containing the guinea pigs is such that the mosquitoes may pass therethrough, the mesh of the larger cages is fine enough to keep the mosquitoes therewithin. The guinea pigs are observed to see whether the mosquitoes bite them on the treated area. The placing of the guinea pig cages into the larger cages is repeated once every hour for a 10 minute period.

For the purposes of the test, the repellent action is regarded as terminated when the guinea pig is bitten by more than one mosquito during the given 10 minute period of observation.

The active compounds, test insect and duration of the repellent effect can be seen from the following Table 1:

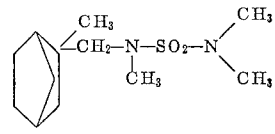
TABLE 1.—REPELLENT-TEST/MOSQUITOES

Insect: *Aedes aegypti.*

	Active compound	Duration of repellent action in hours
(A)	Dimethyl-phthalate (known)	8
(III)	 N-[2,3,3-trimethyl-bicyclo-(2,2,1)-hept-2-yl]-N',N'dimethyl-sulfamide.	21
(IV)	 N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N',N'-dimethyl-sulfamide.	12
(V)	 N—[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-N',N'-dimethyl-sulfamide.	31
(VI)	 N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-N'-methoxy-N'-methyl-sulfamide.	20
(VII)	 N-[(bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-N',N'-dimethyl-sulfamide.	20

The preparation of some of the particular active compounds usable according to the present invention is described by way of illustration, and not limitation, in greater detail in the following:

EXAMPLE 2

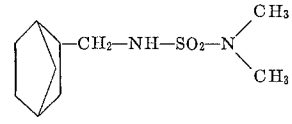


(V')

12.2 g. of dimethyl sulfamic acid chloride are added dropwise at 10–20° C. to a solution of 13.1 g. of N-[(2-methyl-bicyclo-[2,2,1]-hept - 2-yl) - methyl] - N-methyl-amine and 9.5 g. of triethylamine in 50 ml. of methylene chloride. The reaction mixture is heated under reflux for 4 hours, then poured into a concentrated potassium carbonate solution and the resulting organic phase is separated. After distillation of the organic phase, there are obtained 21 g. of N-[(2-methyl-bicyclo-[2,2,1]-hept-2 - yl)-methyl]-N-methyl-N'N'-dimethyl-sulfamide; B.P. 148° C./0.4 mm. Hg.

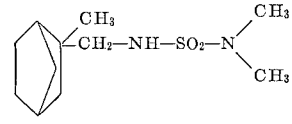
The N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-amine (B.P. 84° C./15 mm. Hg.) used as starting material is obtained by monomethylation of N-(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl-amine which, in turn, is formed by hydrogenation of the Diels-Adler addition product of methacrylonitrile with cyclopentadiene.

The following are obtained by similar methods: N-[(bicyclo-[2,2,1]-hept-2-yl)-methyl] - N',N' - dimethyl-sulfamide; M.P. 66° C.



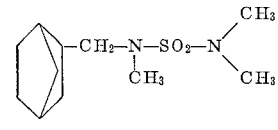
(VIII)

N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl] - N',N'-dimethyl-sulfamide; B.P.150–155° C./0.4 mm. Hg.



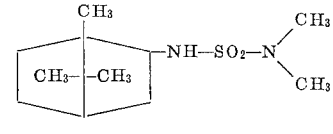
(IV')

N-[(bicyclo[2,2,1]-hept-2-yl)-methyl]-N-methyl - N',N'-dimethyl-sulfamide; B.P. 120° C./0.6 mm. Hg.



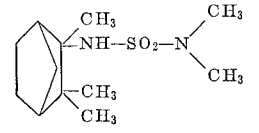
(VII')

N-(1,7,7-trimethyl-bicyclo[2,2,1]-hept - 2 - yl) - N',N'-dimethyl-sulfamide (i.e. N - isobornyl-N',N'-dimethyl-sulfamide); B.P. 170–172° C./0.6 mm. Hg.



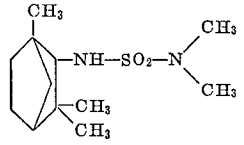
(IX)

N-(2,3,3-trimethyl-bicyclo[2,2,1]-hept - 2 - yl) - N',N'-dimethyl-sulfamide (i.e. N-isocamph-2-yl-N',N'-dimethyl-sulfamide); B.P. 144–146° C./0.4 mm. Hg.



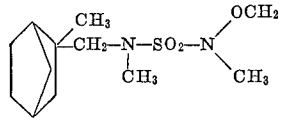
(III')

N-(1,3,3-trimethyl-bicyclo[2,2,1]-hept - 2 - yl) - N',N'-dimethyl-sulfamide (i.e. N' - fench-2-yl-N',N'-dimethyl-sulfamide); B.P. 150–160° C./0.4 mm. Hg.



(X)

EXAMPLE 3



(VI')

28 g. of N-[(2-methyl-bicyclo-[2,2,1]-hept - 2 - yl)-methyl]-N-methyl-amine are added dropwise at 0° C., while stirring vigorously, to 26.5 g. of sulfuryl chloride. The resulting reaction mixture is heated at 65° C. overnight and then cooled; the reaction product is taken up in ether. After distilling off the ether, there remains a residue of 22.3 g. which essentially consists of N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl] - N - methyl-sulfamic acid chloride. The latter is reacted, by the method described in Example 2, with 8 g. of N,O-dimethyl-hydroxylamine in 100 ml. of methylene chloride in the presence of 10 g. of triethylamine. There are obtained in this manner 15 g. of N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl - N' - methyl - N'-methoxy-sulfamide; B.P. 142–146° C./0.4 mm. Hg.

EXAMPLE 4

Using the same procedure as that of Example 2 with corresponding molar amounts of the following starting materials:

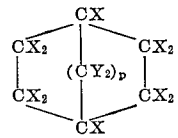
(a) n-propyl sulfamic acid chloride and N-[bicyclo-(2,2,1)-hept-2-yl]-N-isopropyl-amine; and
(b) N-tert.butyl-N-n-butyl-sulfamic acid chloride and N-[(7,7-dimethyl-bicyclo-[2,2,1] - hept-2-yl]-N-n-butyl-amine; and using the same procedure as that of Example 3 with corresponding molar amounts of:
(c) sulfuryl chloride and N-[2-(1',3',4' - trimethyl-bicyclo-[2,2,2]-oct-2'-yl)eth-1-yl] - N - ethyl - amine to form the corresponding sulfamic acid chloride, and thence N-sec.butyl-O-n-propyl-hydroxyamine;

The particular sulfamides, respectively are formed:

(a') N-[bicyclo-(2,2,1)-hept-2-yl]-N-isopropyl - N' - n-propyl-sulfamide;
(b') N-[7,7-dimethyl-bicyclo - [2,2,1] - hept - 2 - yl)-methyl]-N-n-butyl-N'-tert.butyl - N'-n-butyl-sulfamide; and
(c') N - [2-(1',3',4'-trimethyl-bicyclo-[2,2,2]-oct-2'-yl)-eth-1-yl]-N-ethyl-N'-sec.butyl-N'-n-propoxy-sulfamide.

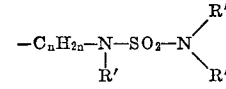
In accordance with a particular feature of the present invention, the following compounds are contemplated herein:

Bicyclo-(2,2,1)-alkyl-substituted sulfamides having the formula:



(Ia)

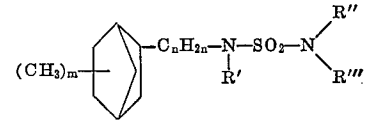
in which one of the symbols X represents the radical:



(Ii)

in which n is a number from 0 to 2, R' is selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, R'' is selected from the group consisting of hydrogen, alkyl having 1 to 4 carbon atoms, and alkoxy having 1 to 3 carbon atoms, R''' is alkyl having 1 to 4 carbon atoms, and p is a number from 1 to 2, with the proviso that where p is 1 then the remaining 9 symbols X and the 2 symbols Y each, respectively, represents a number selected from the group consisting of hydrogen and methyl, with at least 8 and at most 11 of said remaining 9 symbols X and 2 symbols Y being hydrogen, and that where p is 2, then the remaining 9 symbols X and the 4 symbols Y each, respectively, represents a member selected from the group consisting of hydrogen and methyl, with at least 11 and at most 13 of said remaining 9 symbols X and the 4 symbols Y being hydrogen; and

N-[bicyclo-(2,2,1)-hept-2-yl]-sulfamides having the formula:



(IIi)

in which m is a number from 0 to 3, n is a number from 0 to 2, R' is selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, R'' is selected from the group consisting of hydrogen, alkyl having 1 to 4 carbon atoms, and alkoxy having 1 to 3 carbon atoms, and R''' is alkyl having 1 to 4 carbon atoms.

Advantageously, in accordance with the present invention, in the foregoing formulae:

R' represents hydrogen, or alkyl having 1–4 carbon atoms, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec.-butyl, tert.-butyl, especially methyl;
R'' represents hydrogen; or alkyl having 1–4 carbon atoms, such as methyl to tert.-butyl inclusive as noted above; or alkoxy having 1–3 carbon atoms, such as methoxy, ethoxy, n-propoxy and iso-propoxy;
R''' represents alkyl having 1–4 carbon atoms, such as methyl to tert.-butyl inclusive as noted above;
m is a number from 0 to 3 inclusive;
n is a number from 0 to 2 inclusive; and
p is a number from 1 to 2.

In connection with the foregoing, it will be appreciated that where the group $(CH_3)_m$ is concerned, the same preferably contemplatess monomethyl or trimethyl, or of course, otherwise hydrogen; and that with respect to the designation C_nH_{2n}, the same may represent a bond between the ring carbon atom and the adjacent N atom of the adjacent N atom of the sulfamide group where n is 0, or the methylene group where n is 1, or 1,2-ethylene (i.e., dimethylene—CH_2CH_2—) or 1,1-ethylene (i.e., methyl-methylene

where n is 2. Also, in the case of the group $(CH_2)_p$, the same represents an endomethylene (i.e., —CH_2—) where p is 1, or endoethylene (i.e., endo-dimethylene

—CH_2—CH_2)

where p is 2, either of which endomethylene or endoethylene may be substituted with one or more of said $(CH_3)_m$ substituents where m is correspondingly 1, 2 or 3.

It will be realized by the artisan that all of the foregoing compounds contemplated by the present invention possess the desired pest-repellent, especially insect-repellent and acarid-repellent, including mite-repellent, activity, and extremely low phytotoxicity as regards cultivated plants, as well as extremely low toxicity towards warm-blooded animals.

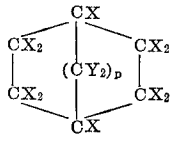
As contemplated herein, the terms "arthropod" and "arthropod-repellent" may be defined as encompassing specifically both insects and acarids within the contem-

plation of their meaning, for convenience in determining the collective aspects of utility herein. Thus, the insects and acarids may be considered herein collectviely as arthropods to be combated collectively in accordance with the invention, and hence the insect-repellent and/or acarid-repellent activity may be termed arthroped-repellent activity, and the concomitant combative or effective amount used in accordance with the invention will be an arthropod-repellent effective amount which in essence means an insect-repellent or acarid-repellent effective amount of the active compound for the desired purpose.

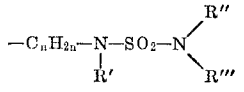
It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention which is to be limited only by the scope of the appended claims.

What is claimed is:

1. Bicyclo-(2,2,1)-alkyl-substituted sulfamide having the formula

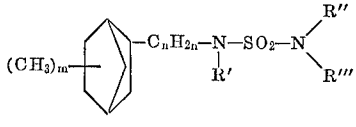


in which one of the symbols X on a carbon atom having two X substituents represents the radical:



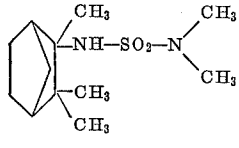
in which n is a number from 0 to 2, R′ is selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, R″ is selected from the group consisting of hydrogen, alkyl having 1 to 4 carbon atoms, and alkoxy having 1 to 3 carbon atoms, R‴ is alkyl having 1 to 4 carbon atoms, and p is a number from 1 to 2, with the proviso that where p is 1 then the remaining 9 symbols X and the 2 symbols Y each, respectively, represents a member selected from the group consisting of hydrogen and methyl, with at least 8 and at most 11 of said remaining 9 symbols X and 2 symbols Y being hydrogen, and that where p is 2, then the remaining 9 symbols X and the 4 symbols Y each, respectively, represents a member selected from the group consisting of hydrogen and methyl, with at least 11 and at most 13 of said remaining 9 symbols X and the 4 symbols Y being hydrogen.

2. Sulfamide according to claim **1** wherein such compound is N-[bicyclo-(2,2,1)-hept-2-yl]-sulfamide having the formula:

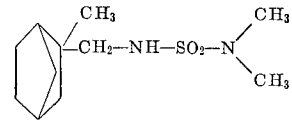


in which m is a number from 0 to 3, n is a number from 0 to 2, R′ is selected from the group consisting of hydrogen and alkyl having 1 to 4 carbon atoms, R″ is selected from the group consisting of hydrogen, alkyl having 1 to 4 carbon atoms, and alkoxy having 1 to 3 carbon atoms, and R‴ is alkyl having 1 to 4 carbon atoms.

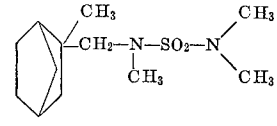
3. Sulfamide according to claim **1** wherein such compound is N-[2,3,3-trimethyl-bicyclo-(2,2,1)-hept-2-yl]-N′,N′-dimethyl-sulfamide having the formula:



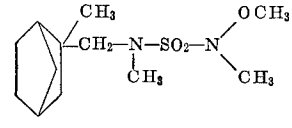
4. Sulfamide according to claim **1** wherein such compound is N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N′,N′-dimethyl-sulfamide having the formula:



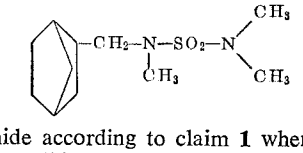
5. Sulfamide according to claim **1** wherein such compound is N-[(2-methyl-bicyclo-[2,2,2]-hept-2-yl)-methyl]-N-methyl-N′,N′ - dimethyl-sulfamide having the formula:



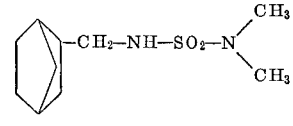
6. Sulfamide according to claim **1** wherein such compound is N-[(2-methyl-bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-N′-methoxy-N′-methyl-sulfamide having the formula:



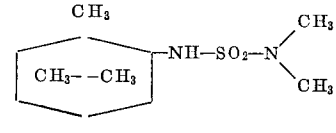
7. Sulfamide according to claim **1** wherein such compound is N-[(bicyclo-[2,2,1]-hept-2-yl)-methyl]-N-methyl-N′,N′-dimethyl-sulfamide having the formula:



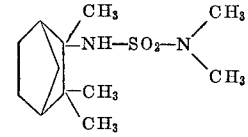
8. Sulfamide according to claim **1** wherein such compound is N-[(bicyclo-[2,2,1]-hept-2-yl)-methyl]-N,N′-dimethyl-sulfamide having the formula:



9. Sulfamide according to claim **1** wherein such compound is N-[1,7,7-trimethyl-bicyclo-(2,2,1)-hept-2-yl]-N′,N′-dimethyl-sulfamide having the formula:



10. Sulfamide according to claim **1** wherein such compounds is N-[2,3,3-trimethyl-bicyclo-(2,2,1)-hept-2-yl]-N′,N′-dimethyl-sulfamide having the formula:



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U.S. Cl. X.R.

260—543, 556, 563; 424—299, 321

Farben 1249
PF/ey
PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,513,182 Dated May 19, 1970

Inventor(s) Hartmund Wollweber, Rudolf Hiltmann, Wolfgang Behrenz, Gerhard Müller

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, lines 26 and 27, "infestances" should be --infestans--.

Column 4, line 45, "whic his" should be -- which is --.

Column 8, lines 50 and 51, delete "of the adjacent N atom".

SIGNED AND SEALED
DEC 29 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents